



UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Deputy Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the French and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the specification in French filed with the application for a patent in the U.S.A. on *April 1st, 2004* under the number *10/814,585*.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

A handwritten signature in cursive script, appearing to read "Charles Edward Sitch", written over a horizontal line.

For and on behalf of RWS Group Ltd

The 2nd day of July 2004



**COMPOSITION FOR DYEING HUMAN KERATIN MATERIALS,
COMPRISING A FLUORESCENT DYE AND A PARTICULAR
SEQUESTERING AGENT, PROCESS THEREFOR AND USE THEREOF**

5 The invention relates to a composition
comprising at least one fluorescent dye and at least
one particular sequestering agent, and also to
processes and a device for using these compositions.
The present invention similarly relates to the use of a
10 composition comprising at least one fluorescent dye and
at least one particular sequestering agent, to dye with
a lightening effect human keratin materials and more
particularly keratin fibres such as artificially dyed
or pigmented hair, and also coloured skin.

15 It is common for individuals with coloured
skin to wish to lighten their skin and for this purpose
to use cosmetic or dermatological compositions
containing bleaching agents.

 The substances most commonly used as
20 bleaching agent are hydroquinone and its derivatives,
kojic acid and its derivatives, azelaic acid, arbutin
and its derivatives, alone or in combination with other
active agents.

 However, these agents are not without their
25 drawbacks. In particular, they need to be used for a
long time and in large amounts in order to obtain a
bleaching effect on the skin. No immediate effect is
observed on applying compositions comprising them.

In addition, hydroquinone and its derivatives are used in an amount that is effective to produce a visible bleaching effect. In particular, hydroquinone is known for its cytotoxicity towards melanocytes.

5 Moreover, kojic acid and its derivatives have the drawback of being expensive and consequently of not being able to be used in large amount in products for commercial mass distribution.

 There is thus still a need for cosmetic
10 compositions that allow a lighter, uniform, homogeneous tone of natural appearance to be obtained, these compositions having satisfactory transparency after application to the skin.

 In the field of haircare, there are mainly
15 two major types of hair dyeing.

 The first is semi-permanent dyeing or direct dyeing, which uses dyes capable of giving the hair's natural colour a more or less pronounced modification that withstands shampooing several times. These dyes
20 are known as direct dyes and may be used in two different ways. The dyeing may be performed by applying the composition containing the direct dye(s) directly to the keratin fibres, or by applying a mixture, prepared extemporaneously, of a composition containing
25 the direct dye(s) with a composition containing an oxidizing bleaching agent, which is preferably aqueous hydrogen peroxide solution. Such a process is then termed "lightening direct dyeing".

The second is permanent dyeing or oxidation dyeing. This is performed with "oxidation" dye precursors, which are colourless or weakly coloured compounds which, once mixed with oxidizing products, at
5 the time of use, can give rise to coloured compounds and dyes via a process of oxidative condensation. It is often necessary to combine one or more direct dyes with the oxidation bases and couplers in order to neutralize or attenuate the shades with too much of a red, orange
10 or golden glint or, on the contrary, to accentuate these red, orange or golden glints.

Among the available direct dyes, nitrobenzene direct dyes are not sufficiently strong, and indo- amines, quinone dyes and natural dyes have low affinity
15 for keratin fibres and consequently lead to dyeing that is not sufficiently fast with respect to the various treatments to which the fibres may be subjected, and in particular with respect to shampooing.

In addition, there is a need to obtain a
20 lightening effect on human keratin fibres. This lightening is conventionally obtained via a process of bleaching the melanins of the hair via an oxidizing system generally consisting of hydrogen peroxide optionally combined with persalts. This bleaching
25 system has the drawback of degrading the keratin fibres and of impairing their cosmetic properties.

The object of the present invention is to solve the problems mentioned above and especially to

propose a composition that has good dyeing affinity for keratin materials and especially keratin fibres, good resistance properties with respect to external agents, and in particular with respect to shampooing, and that
5 also makes it possible to obtain lightening without impairing the treated material, more particularly the keratin fibre.

It has thus been found, surprisingly and unexpectedly, that the use of fluorescent dyes, in
10 particular those in the orange range, in the presence of particular sequestering agents, allows these objectives to be achieved.

A first subject of the present invention is thus a composition comprising, in a cosmetically
15 acceptable medium, at least one fluorescent dye that is soluble in the said medium and at least one complexing agent chosen from hydroxycarboxylic acids and polycarboxylic acids, and the monovalent or divalent alkali metal, alkaline-earth metal, transition metal,
20 organic amine or ammonium salts thereof, alone or as mixtures; the composition not comprising, as fluorescent agent, 2-[2-(4-dialkylamino)phenylethenyl]-1-alkylpyridinium in which the alkyl radical of the pyridinium nucleus represents a methyl or ethyl radical
25 and that of the benzene nucleus represents a methyl radical, and in which the counterion is a halide.

A second subject of the invention concerns a process for dyeing human keratin fibres with a

lightening effect, in which the following steps are performed:

- a) a composition according to the invention is applied to the said fibres, for a time that is sufficient to develop the desired coloration and lightening,
- b) the fibres are optionally rinsed,
- c) the fibres are optionally washed with shampoo and rinsed,
- d) the fibres are dried or are left to dry.

Another subject of the invention concerns the use of a composition comprising, in a cosmetically acceptable medium, at least one fluorescent dye that is soluble in the said medium and at least one complexing agent chosen from hydroxycarboxylic acids and polycarboxylic acids, and the monovalent or divalent alkali metal, alkaline-earth metal, transition metal, organic amine or ammonium salts thereof, alone or as mixtures, to dye with a lightening effect human keratin materials.

A multi-compartment device for dyeing and lightening keratin fibres, comprising at least one compartment containing the composition according to the invention, and at least one other compartment containing a composition containing at least one oxidizing agent, constitutes a final subject of the invention.

The compositions of the invention in

particular allow an increased fluorescent effect and a lightening effect that is greater than that obtained with the fluorescent dye used alone.

Better resistance of the result with respect
5 to washing or shampooing is also found.

However, other characteristics and advantages of the present invention will emerge more clearly on reading the description and the examples that follow.

Unless otherwise indicated, the limits of the
10 ranges of values that are given in the description are included within these ranges.

As has been mentioned previously, the composition according to the invention comprises at least one fluorescent dye and at least one particular
15 sequestering agent.

For the purposes of the present invention, the term "fluorescent dye" means a dye which is a molecule that colours by itself, and thus absorbs light in the visible spectrum and possibly in the ultraviolet
20 spectrum (wavelengths ranging from 360 to 760 nanometres), but which, in contrast with a standard dye, converts the absorbed energy into fluorescent light of longer wavelength emitted in the visible region of the spectrum.

25 A fluorescent dye according to the invention is to be differentiated from an optical brightener. Optical brighteners, which are also known as brighteners, fluorescent brighteners, fluorescent

brightening agents, fluorescent whitening agents, whiteners or fluorescent whiteners, are colourless transparent compounds, which do not dye because they do not absorb light in the visible region, but only in the
5 ultraviolet region (wavelengths ranging from 200 to 400 nanometres), and convert the absorbed energy into fluorescent light of longer wavelength emitted in the visible region of the spectrum; the colour impression is then generated solely by purely fluorescent light
10 that is predominantly blue (wavelengths ranging from 400 to 500 nanometres).

Finally, the fluorescent dye used in the composition is soluble in the medium of the composition. It should be pointed out that the
15 fluorescent dye differs therein from a fluorescent pigment, which itself is insoluble in the medium of the composition.

More particularly, the fluorescent dye used in the context of the present invention, which is
20 optionally neutralized, is soluble in the medium of the composition to at least 0.001 g/l, more particularly at least 0.5 g/l, preferably at least 1 g/l and, according to one even more preferred embodiment, at least 5 g/l at a temperature of between 15 and 25°C.

25 Moreover, according to one characteristic of the invention, the composition does not comprise, as fluorescent dye, a 2-[2-(4-dialkylamino)phenylethenyl]-1-alkylpyridinium in which the alkyl radical of the

pyridinium nucleus represents a methyl or ethyl radical and that of the benzene nucleus represents a methyl radical, and in which the counterion is a halide.

In accordance with an even more particular
5 embodiment of the invention, the composition does not comprise, as fluorescent dye, a compound chosen from azo, azomethine or methine monocationic heterocyclic fluorescent dyes.

The fluorescent dyes preferably used
10 according to the present invention are dyes in the orange range.

Preferably, the fluorescent dyes of the invention lead to a reflectance maximum that is in the wavelength range from 500 to 650 nanometres and
15 preferably in the wavelength range from 550 to 620 nanometres.

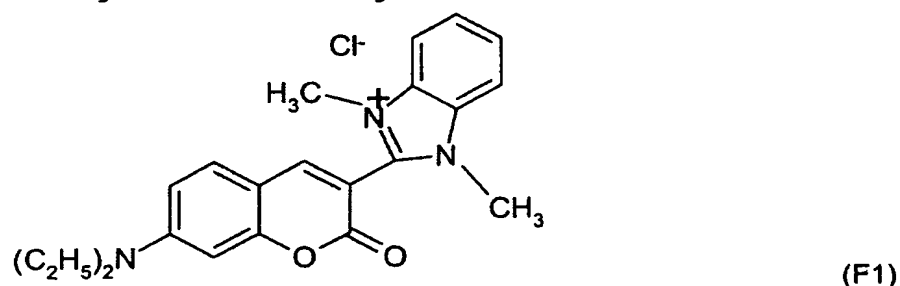
Some of the fluorescent dyes according to the present invention are compounds that are known per se.

As examples of fluorescent dyes that may be
20 used, mention may be made of the fluorescent dyes belonging to the following families: naphthalimides; cationic or non-cationic coumarins; xanthenodiquinolizines (such as, especially, sulphorhodamines); azaxanthenes; naphtholactams; azlactones; oxazines;
25 thiazines; dioxazines; polycationic fluorescent dyes of azo, azomethine or methine type, alone or as mixtures, and preferably belonging to the following families: naphthalimides; cationic or non-cationic coumarins;

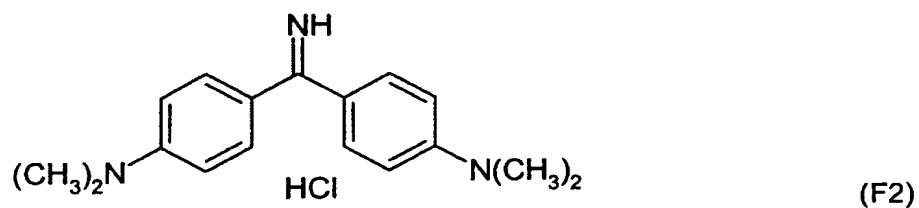
azaxanthenes; naphtholactams; azlactones; oxazines;
thiazines; dioxazines; polycationic fluorescent dyes of
azo, azomethine or methine type, alone or as mixtures.

More particularly, the following may be
5 mentioned among the above dyes:

- Brilliant Yellow B6GL sold by the company Sandoz and
having the following structure:

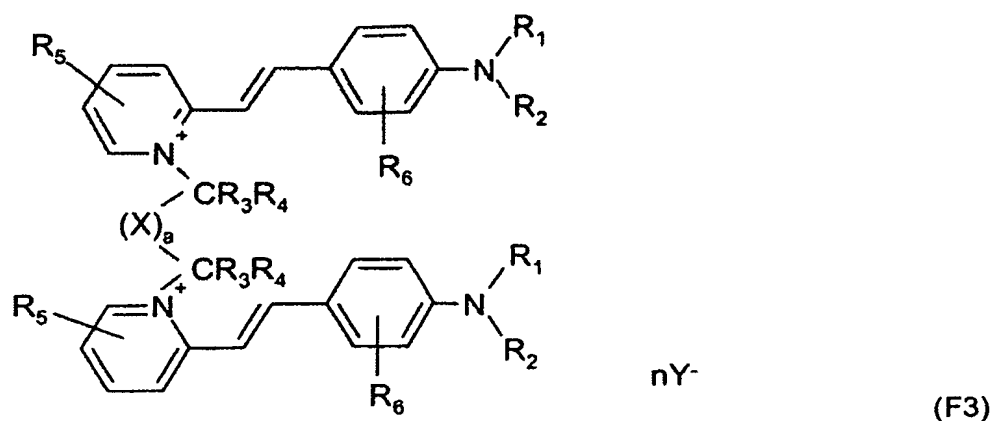


- Basic Yellow 2, or Auramine O, sold by the companies
10 Prolabo, Aldrich or Carlo Erba and having the following
structure:



4,4'-(imidocarbonyl)bis(N,N-dimethylaniline) monohydro-
chloride - CAS number 2465-27-2.

15 Mention may also be made of the compounds
having the following formula:



in which:

R_1 and R_2 , which may be identical or different,
represent:

- 5 • a hydrogen atom;
- a linear or branched alkyl radical containing
 1 to 10 carbon atoms and preferably from 1 to
 4 carbon atoms, optionally interrupted and/or
10 substituted with at least one hetero atom
 and/or group containing at least one hetero
 atom and/or substituted with at least one
 halogen atom;
- an aryl or arylalkyl radical, the aryl group
 containing 6 carbon atoms and the alkyl
15 radical containing 1 to 4 carbon atoms; the
 aryl radical optionally being substituted
 with one or more linear or branched alkyl
 radicals containing 1 to 4 carbon atoms
 optionally interrupted and/or substituted
20 with at least one hetero atom and/or group
 containing at least one hetero atom and/or

substituted with at least one halogen atom;

- 5 R_1 and R_2 may optionally be linked so as to form a heterocycle with the nitrogen atom and may contain one or more other hetero atoms, the heterocycle optionally being substituted with at least one linear or branched alkyl radical preferably containing from 1 to 4 carbon atoms and optionally being interrupted and/or substituted with at least one hetero atom and/or group containing at least one hetero atom and/or substituted with at least one halogen atom;

10
- 15 R_1 or R_2 may optionally be engaged in a heterocycle containing the nitrogen atom and one of the carbon atoms of the phenyl group bearing the said nitrogen atom;

R_3 and R_4 , which may be identical or different, represent a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms;

- 20 R_5 , which may be identical or different, represent a hydrogen atom, a halogen atom or a linear or branched alkyl radical containing 1 to 4 carbon atoms, optionally interrupted with at least one hetero atom;
- 25 R_6 , which may be identical or different, represent a hydrogen atom; a halogen atom; a linear or branched alkyl radical containing 1 to 4 carbon atoms, optionally substituted and/or interrupted with at least one hetero atom and/or group bearing at least one

hetero atom and/or substituted with at least one
halogen atom;

X represents:

- 5 • a linear or branched alkyl radical containing
 1 to 14 carbon atoms or an alkenyl radical
 containing 2 to 14 carbon atoms, optionally
 interrupted and/or substituted with at least
 one hetero atom and/or group containing at
10 least one hetero atom and/or substituted with
 at least one halogen atom;
- a 5- or 6-membered heterocyclic radical
 optionally substituted with at least one
 linear or branched alkyl radical containing 1
15 to 14 carbon atoms, optionally substituted
 with at least one hetero atom; with at least
 one linear or branched aminoalkyl radical
 containing 1 to 4 carbon atoms, optionally
20 substituted with at least one hetero atom;
 with at least one halogen atom;
- a fused or non-fused aromatic or diaromatic
 radical, optionally separated by an alkyl
 radical containing 1 to 4 carbon atoms, the
 aryl radical(s) optionally being substituted
25 with at least one halogen atom or with at
 least one alkyl radical containing 1 to 10
 carbon atoms optionally substituted and/or
 interrupted with at least one hetero atom
 and/or group bearing at least one hetero

atom;

- a dicarbonyl radical;
- the group X possibly bearing one or more cationic charges;

5 a being equal to 0 or 1;

Y^- , which may be identical or different, representing an organic or inorganic anion;

n being an integer at least equal to 2 and at most equal to the number of cationic charges present in the

10 fluorescent compound.

It should be recalled that the term "hetero atom" represents an oxygen or nitrogen atom.

Among the groups bearing such atoms that may be mentioned, inter alia, are hydroxyl, alkoxy, carbonyl, amino, ammonium, amido ($-N-CO-$) and carboxyl ($-O-CO-$ or $-CO-O-$) groups.

As regards the alkenyl groups, they contain one or more unsaturated carbon-carbon bonds ($-C=C-$) and preferably only one carbon-carbon double bond.

20 In this general formula, the radicals R_1 and R_2 , which may be identical or different, more particularly represent:

- a hydrogen atom;
- an alkyl radical containing 1 to 10 carbon atoms, especially 1 to 6 carbon atoms and preferably 1 to 4 carbon atoms, optionally interrupted with an oxygen atom or optionally substituted with at least one hydroxyl, amino

25

or ammonium radical or a chlorine or fluorine atom;

- a benzyl or phenyl radical optionally substituted with an alkyl or alkoxy radical containing 1 to 4 carbon atoms and preferably 1 or 2 carbon atoms;
- with the nitrogen atom, a heterocyclic radical of the pyrrolo, pyrrolidino, imidazolino, imidazolo, imidazolium, pyrazolino, piperazino, morpholino, morpholo, pyrazolo or triazolo type, optionally substituted with at least one linear or branched alkyl radical containing 1 to 4 carbon atoms optionally interrupted and/or substituted with a nitrogen and/or oxygen atom and/or group bearing a nitrogen and/or oxygen atom.

As regards the abovementioned amino or ammonium radicals, the radicals borne by the nitrogen atom may be identical or different and may more particularly represent a hydrogen atom, a C₁-C₁₀ and preferably C₁-C₄ alkyl radical or an arylalkyl radical in which, more especially, the aryl radical contains 6 carbon atoms and the alkyl radical contains 1 to 10 carbon atoms and preferably 1 to 4 carbon atoms.

According to one advantageous embodiment of the invention, the radicals R₁ and R₂, which may be identical or different, represent a hydrogen atom; a

linear or branched C₁-C₆ alkyl radical; a C₂-C₆ alkyl radical substituted with a hydroxyl radical; a C₂-C₆ alkyl radical bearing an amino or ammonium group; a C₂-C₆ chloroalkyl radical; a C₂-C₆ alkyl radical interrupted with an oxygen atom or a group bearing an oxygen atom (for example ester); an aromatic radical, for instance phenyl, benzyl or 4-methylphenyl; a heterocyclic radical such as pyrrolo, pyrrolidino, imidazolo, imidazolino, imidazolium, piperazino, morpholo, morpholino, pyrazolo or triazolo radicals, optionally substituted with at least one C₁-C₆ alkyl or aromatic radical.

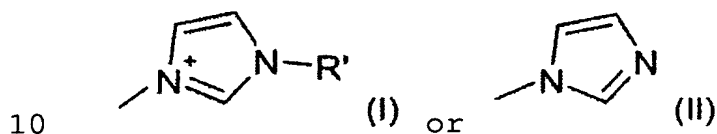
Preferably, the radicals R₁ and R₂, which may be identical or different, represent a hydrogen atom, a linear or branched C₁-C₆ alkyl radical such as methyl, ethyl, n-butyl or n-propyl radicals; 2-hydroxyethyl; an alkyltrimethylammonium or alkyltriethylammonium radical, the alkyl radical being a linear C₂-C₆ alkyl radical; a (di)alkylmethylamino or (di)alkylethylamino radical, the alkyl radical being a linear C₁-C₆ alkyl radical; -CH₂CH₂Cl; -(CH₂)_n-OCH₃ or -(CH₂)_n-OCH₂CH₃ with n being an integer ranging from 2 to 6; -CH₂CH₂-OCOCH₃; -CH₂CH₂COOCH₃.

Preferably, the radicals R₁ and R₂, which may be identical or different, and which are preferably identical, represent a methyl radical or an ethyl radical.

The radicals R₁ and R₂, which may be identical

or different, may also represent a heterocyclic radical of the pyrrolidino, 3-aminopyrrolidino, 3-(dimethyl)-aminopyrrolidino, 3-(trimethyl)aminopyrrolidino, 2,5-dimethylpyrrolo, 1H-imidazolo, 4-methylpiperazino, 4-benzylpiperazino, morpholo, 3,5-(tert-butyl)-1H-pyrazolo, 1H-pyrazolo or 1H-1,2,4-triazolo type.

The radicals R_1 and R_2 , which may be identical or different, may also represent radicals linked so as to form a heterocycle of formulae (I) and (II) below:



in which R' represents a hydrogen atom or a C_1 - C_3 alkyl radical, $-CH_2CH_2OH$, $-CH_2CH_2OCH_3$.

In accordance with a more particular embodiment of the invention, R_5 , which may be identical or different, represent a hydrogen atom, a fluorine or chlorine atom or a linear or branched alkyl radical containing 1 to 4 carbon atoms optionally interrupted with an oxygen or nitrogen atom.

It is pointed out that the substituent R_5 , if it is other than hydrogen, is advantageously in position(s) 3 and/or 5 relative to the carbon of the ring bearing the nitrogen substituted with the radicals R_1 and R_2 , and preferably in position 3 relative to that carbon.

Advantageously, the radicals R_5 , which may be identical or different, represent a hydrogen atom; a

linear or branched C_1-C_4 alkyl radical; $-O-R_{51}$ with R_{51} representing a linear C_1-C_4 alkyl radical; $-R_{52}-O-CH_3$ with R_{52} representing a linear C_2-C_3 alkyl radical; $-R_{53}-N(R_{54})_2$ in which R_{53} represents a linear C_2-C_3 alkyl radical and R_{54} , which may be identical or different, represent a hydrogen atom or a methyl radical.

Preferably, R_5 , which may be identical or different, represent hydrogen, a methyl or a methoxy, and R_5 preferentially represents a hydrogen atom.

According to one particular embodiment, the radicals R_6 , which may be identical or different, represent a hydrogen atom; a linear or branched C_1-C_4 alkyl radical; $-X$ with X representing a chlorine, bromine or fluorine atom; $-R_{61}-O-R_{62}$ with R_{61} representing a linear C_2-C_3 alkyl radical and R_{62} representing a methyl radical; $-R_{63}-N(R_{64})_2$ with R_{63} representing a linear C_2-C_3 alkyl radical and R_{64} , which may be identical or different, representing a hydrogen atom or a methyl radical; $-N(R_{65})_2$ in which R_{65} , which may be identical or different, represent a hydrogen atom or a linear C_2-C_3 alkyl radical; $-NHCOR_{66}$ with R_{66} representing a C_1-C_2 alkyl radical, a C_1-C_2 chloroalkyl radical, a radical $-R_{67}-NH_2$ or $-R_{67}-NH(CH_3)$ or $-R_{67}-N(CH_3)_2$ or $-R_{67}-N^+(CH_3)_3$ or $-R_{67}-N^+(CH_2CH_3)_3$ with R_{67} representing a C_1-C_2 alkyl radical.

It is pointed out that the substituent R_6 , if it is other than hydrogen, is preferably in position 2 and/or 4 relative to the nitrogen atom of the

pyridinium ring, and preferentially in position 4 relative to that nitrogen atom.

More particularly, these radicals R_6 , which may be identical or different, represent a hydrogen atom or a methyl or ethyl radical, and R_6 preferably represents a hydrogen atom.

As regards the radicals R_3 and R_4 , these radicals, which may be identical or different, advantageously represent a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms and more especially a methyl radical. Preferably, R_3 and R_4 each represent a hydrogen atom.

As mentioned above, X represents:

- a linear or branched alkyl radical containing 1 to 14 carbon atoms or an alkenyl radical containing 2 to 14 carbon atoms, optionally interrupted and/or substituted with at least one hetero atom, with at least one group bearing at least one hetero atom and/or with at least one halogen atom;
- a 5- or 6-membered heterocyclic radical optionally substituted with at least one linear or branched alkyl radical containing 1 to 14 carbon atoms, with at least one linear or branched aminoalkyl radical containing 1 to 4 carbon atoms, optionally substituted with at least one hetero atom; with at least one halogen atom;

- a fused or non-fused aromatic or diaromatic radical, optionally separated by an alkyl radical containing 1 to 4 carbon atoms, the aryl radical(s) optionally being substituted with at least one halogen atom or with at least one alkyl radical containing 1 to 10 carbon atoms optionally substituted and/or interrupted with at least one hetero atom and/or group bearing at least one hetero atom;
- a dicarbonyl radical.

In addition, it is indicated that the group X may bear one or more cationic charges.

Thus, X may represent a linear or branched alkyl radical containing 1 to 14 carbon atoms or an alkenyl radical containing 2 to 14 carbon atoms, and may be substituted and/or interrupted with one or more oxygen and/or nitrogen atoms, and/or with one or more groups bearing at least one hetero atom, and/or with a fluorine or chlorine atom.

Among the groups of this type that may be mentioned most particularly are hydroxyl, alkoxy (especially with a radical R of the C₁-C₄ alkyl type), amino, ammonium, amido, carbonyl and carboxyl groups (-COO- or -O-CO-) especially with a radical of alkyloxy type.

It should be noted that the nitrogen atom, if it is present, may be in a quaternized or non-

quaternized form. In this case, the other radical or the other two radicals borne by the quaternized or non-quaternized nitrogen atom is(are) identical or different and may be a hydrogen atom or a C₁-C₄ alkyl radical, preferably methyl.

According to another variant, the group X represents a 5- or 6-membered heterocyclic radical of the imidazolo, pyrazolo, triazino or pyridino type, optionally substituted with at least one linear or branched alkyl radical containing 1 to 14 carbon atoms, more particularly 1 to 10 carbon atoms and preferably from 1 to 4 carbon atoms; with at least one linear or branched aminoalkyl radical containing 1 to 10 carbon atoms and preferably from 1 to 4 carbon atoms, optionally substituted with a group containing at least one hetero atom (preferably a hydroxyl radical), or with a halogen atom. It should be noted that the amino group is preferably linked to the heterocycle.

In accordance with another possibility, the group X represents an aromatic radical (preferably containing 6 carbon atoms) or fused or non-fused diaromatic radical (especially containing from 10 to 12 carbon atoms), possibly separated by an alkyl radical containing 1 to 4 carbon atoms, the aryl radical(s) optionally being substituted with at least one halogen atom and/or with at least one alkyl radical containing 1 to 10 carbon atoms and preferably 1 to 4 carbon atoms, optionally interrupted with at least

one oxygen and/or nitrogen atom and/or a group containing at least one hetero atom (for instance a carbonyl, carboxyl, amido, amino or ammonium radical).

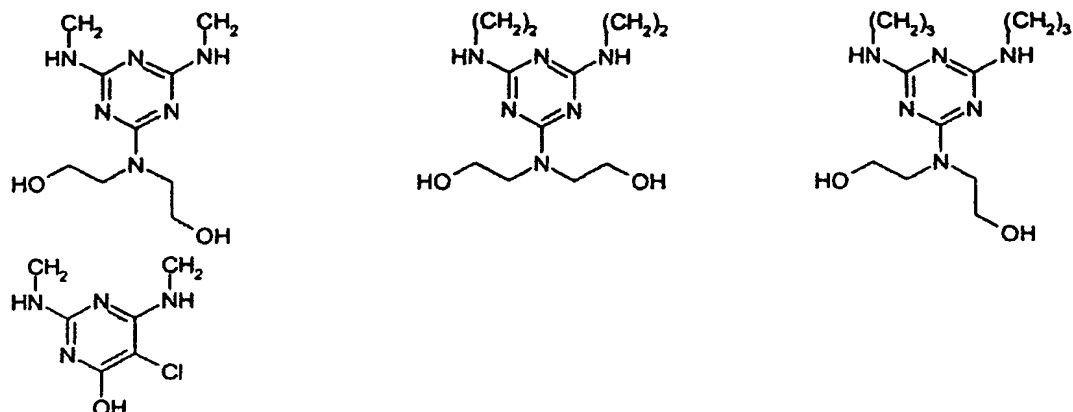
It should be noted that the aromatic radical, preferably a phenyl radical, is linked to the groups CR_3R_4 via bonds in positions 1,2; 1,3 or 1,4 and preferably in positions 1,3 and 1,4. If the phenyl radical linked via bonds in positions 1,4 bears one or two substituents, this or these substituent(s) is(are) preferably located in position 1,4 relative to one of the groups CR_3R_4 . If the phenyl radical linked via bonds in positions 1,3 bears one or two substituent(s), this or these substituent(s) is (are) preferably located in position 1 or 3 relative to one of the groups CR_3R_4 .

In the case where the radical is diaromatic, it is preferably non-fused and comprises two phenyl radicals possibly separated by a single bond (i.e. a carbon of each of the two rings) or by an alkyl radical, preferably of CH_2 or $C(CH_3)_2$ type. Preferably, the aromatic radicals do not bear a substituent. It should be noted that the said diaromatic radical is linked to the groups CR_3R_4 via bonds in positions 4,4'.

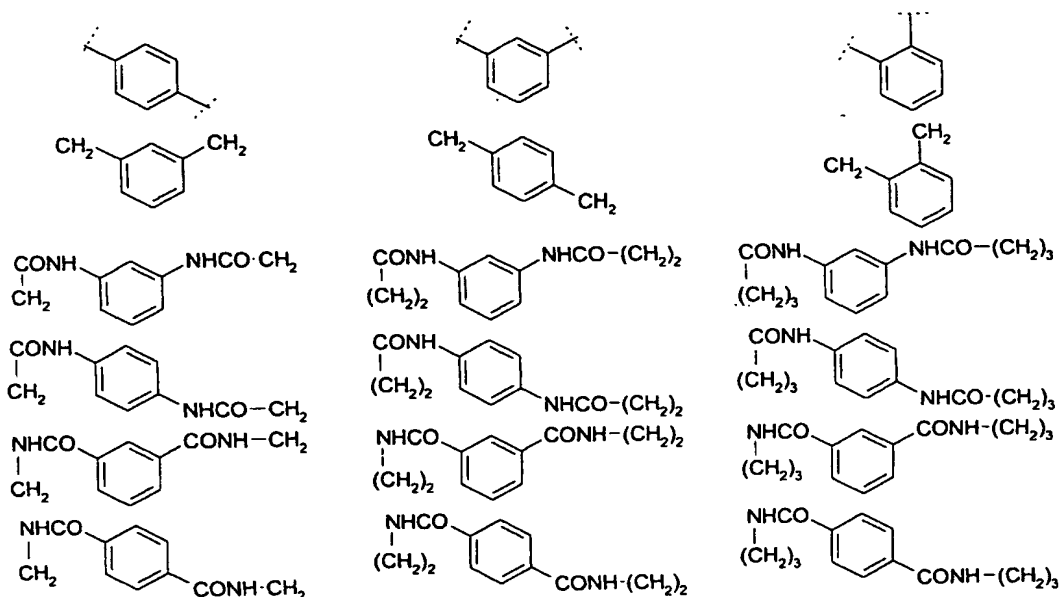
As examples of groups X that are suitable, mention may be made especially of linear or branched alkyl radicals containing 1 to 13 carbon atoms, such as methylene, ethylene, propylene, isopropylene, n-butylene, pentylene and hexylene; 2-hydroxypropylene and 2-hydroxy-n-butylene; C_1 - C_{13} alkylene radicals

substituted or interrupted with one or more nitrogen and/or oxygen atoms, and/or groups bearing at least one hetero atom (hydroxyl, amino, ammonium, carbonyl or carboxyl, for example), such as $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$,
 5 1,6-dideoxy-d-mannitol, $-\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2-$,
 $-\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_6\text{N}^+(\text{CH}_3)_2-\text{CH}_2\text{CH}_2-$, $\text{CO}-\text{CO}-$, 3,3-di-
 methylpentylene, 2-acetoxyethylene, butylene-1,2,3,4-
 tetraol; $-\text{CH}=\text{CH}-$; aromatic or diaromatic radicals
 substituted with one or more alkyl radicals, with one
 10 or more groups bearing at least one hetero atom and/or
 with one or more halogen atoms, such as 1,4-phenylene,
 1,3-phenylene, 1,2-phenylene, 2,6-fluorobenzene,
 4,4'-biphenylene, 1,3-(5-methylbenzene), 1,2-bis(2-
 methoxy)benzene, bis(4-phenyl)methane, methyl
 15 3,4-benzoate and 1,4-bis(amidomethyl)phenyl; radicals
 of heterocyclic type, for instance pyridine or a
 derivative thereof such as 2,6-bispyridine, imidazole,
 imidazolium or triazine.

According to a more particular embodiment of
 20 the invention, X represents a linear or branched C_1-C_{13}
 alkyl radical; $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$; $-\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2-$;
 $-\text{CH}_2\text{CH}_2-\text{OCOCH}_2-$; $-\text{CH}_2\text{CH}_2\text{COOCH}_2-$; $-\text{Ra}-\text{O}-\text{Rb}-$ with Ra
 representing a linear C_2-C_6 alkyl radical and Rb
 representing a linear C_1-C_2 alkyl radical; $-\text{Rc}-\text{N}(\text{Rd})-\text{Re}-$
 25 with Rc representing a C_2-C_9 alkyl radical, Rd
 representing a hydrogen atom or a C_1-C_2 alkyl radical
 and Re representing a C_1-C_6 alkyl radical;
 $-\text{Rf}-\text{N}^+(\text{Rg})_2-\text{Rh}-$ with Rf representing a linear C_2-C_9 alkyl



According to another possibility, X may represent the divalent aromatic radicals below:



5 In the general formula of these fluorescent compounds, Y^- represents an organic or inorganic anion. If there are several anions Y^- , these anions may be identical or different.

10 Among the anions of mineral origin that may be mentioned, without wishing to be limited thereto, are anions derived from halogen atoms, such as chlorides, preferably, or iodides, sulphates or

bisulphates, nitrates, phosphates, hydrogen phosphates, dihydrogen phosphates, carbonates and bicarbonates.

Among the anions of organic origin that may be mentioned are anions derived from the salts of

5 saturated or unsaturated, aromatic or non-aromatic monocarboxylic or polycarboxylic, sulphonic or sulphuric acids, optionally substituted with at least one hydroxyl or amino radical, or halogen atoms. Non-limiting examples that are suitable for use include

10 acetates, hydroxyacetates, aminoacetates, (tri)chloroacetates, benzoxyacetates, propionates and derivatives bearing a chlorine atom, fumarates, oxalates, acrylates, malonates, succinates, lactates, tartrates, glycolates, citrates, benzoates and derivatives bearing

15 a methyl or amino radical, alkyl sulphates, tosylates, benzenesulphonates, toluenesulphonates, etc.

Preferably, the anion(s) Y, which may be identical or different, is(are) chosen from chloride, sulphate, methosulphate and ethosulphate.

20 Finally, the integer n is at least equal to 2 and at most equal to the number of cationic charges present in the fluorescent compound.

Preferably, the fluorescent compounds that have just been described in detail are symmetrical

25 compounds.

These compounds may be synthesized by reacting, in a first step, α -picoline with a reagent containing two leaving groups that may be chosen from

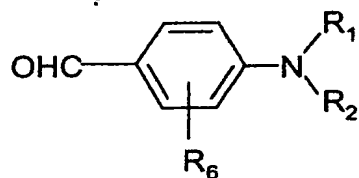
halogen atoms, preferably bromine, or optionally chlorine, or groups of tolylsulphonyl or methylsulphonyl type.

This first step may take place in the presence of a solvent, although this is not obligatory, for instance dimethylformamide.

The number of moles of α -picoline is generally in the region of 2 per mole of reagent containing the leaving groups.

In addition, the reaction is usually performed at the reflux temperature of the reagent and/or of the solvent if a solvent is present.

The product derived from this first step is then placed in contact with a corresponding aldehyde having the following formula:



in which R_1 , R_2 and R_6 have the same meanings as indicated above.

In this case also, the reaction may be performed in the presence of a suitable solvent, preferably at reflux.

It should be noted that the radicals R_1 and R_2 of the aldehyde may have the meaning indicated in the general formula detailed previously.

It is also possible to use an aldehyde for

which the said radicals represent hydrogen atoms and to perform, in accordance with standard methods, the substitution of these hydrogen atoms with suitable radicals as described in the general formula once the
5 second step is complete.

Reference may be made especially to syntheses as described in US 4 256 458.

The fluorescent dye(s) present in the composition according to the invention advantageously
10 represent(s) from 0.01% to 20% by weight, more particularly from 0.05% to 10% by weight and preferably from 0.1% to 5% by weight, relative to the total weight of the composition.

As mentioned previously, the composition also
15 comprises at least one complexing agent chosen from hydroxycarboxylic acids, polycarboxylic acids and the alkali metal, alkaline-earth metal, transition metal, organic amine or ammonium salts thereof, alone or as mixtures.

20 Examples of monovalent cations that may be mentioned include cations of alkali metals such as sodium or potassium.

Mention may also be made of monovalent cations derived from organic amines, such as primary,
25 secondary or tertiary amines, or from alkanolamines. The said amines contain one or more radicals, which may be identical or different, of linear or branched C1-C20 alkyl type, optionally containing a hetero atom, for

instance oxygen. The cations derived from quaternary ammonium, more particularly containing four radicals, which may be identical or different, corresponding to the definition given above, are also suitable.

5 Examples of divalent cations that may be mentioned include divalent cations of alkaline-earth metals such as calcium or magnesium, or of transition metals (metals comprising an incomplete d subshell), more particularly in oxidation state II, for instance
10 the divalent cobalt, iron, manganese, zinc or copper cation.

More particularly, the sequestering agents of hydroxycarboxylic type correspond to the following formula (A): $R-(CHOH)_4-CO_2X$, in which R represents a
15 CH_2OH or CO_2X group and X represents a hydrogen or a monovalent or divalent cation. This formula includes all the enantiomers and all the diastereoisomers of these compounds.

As regards the sequestering agents of
20 polycarboxylic type, they more particularly correspond to compounds of the following formula (B):
 $R-N(Y)(CH(R')CO_2X)$, in which Y represents a hydrogen atom or a group $CH(R')CO_2X$; R represents a hydrogen atom or a group (a) $-CH(CO_2X)-(CH_2)_nCO_2X$, (b) $-(CH_2)_nOH$,
25 (c) $-CH(R'')CO_2X$, (d) $-(CH_2)_n-N(COR'')-CH_2CO_2X$, (e) $-(CH_2)_n-N(CH_2CO_2X)CH_2CO_2X$ and (f) $-(CH_2)_nNH-CH(CO_2X)CH_2CO_2X$, in which R' represents a hydrogen atom or a group CH_2CO_2X ; R'' represents a linear or branched C_1-C_{30} or cyclic C_3-

C₃₀ alkyl group, n is an integer between 1 and 5, and X represents a hydrogen atom or a monovalent or divalent cation as defined in the context of formula (A).

According to one particular embodiment, n is
5 equal to 2.

Among the sequestering compounds that may be used, the following are particularly suitable:

Formula (A): gluconic acid, mucic acid (or galactaric acid), glucaric acid, mannaric acid, salts thereof, and
10 mixtures thereof;

Formula (B):

- compounds containing four carboxylic acid or salt functions, when R represents a hydrogen atom and R' represents a group -CH₂-CO₂X, or when R represents a
15 group -CH(CO₂X)-(CH₂)₂-CO₂X and R' represents a hydrogen atom;
- compounds comprising three carboxylic acid or salt functions, when R represents a group -CH(CH₃)-CO₂X and R' represents a hydrogen atom, or when R
20 represents a group -(CH₂)₂-N(COR'')-CH₂-CO₂X and R' represents a hydrogen atom.

Methylglycinediacetic acid, N-lauroylethylenediamine-N,N',N'-triacetic acid, iminodisuccinic acid, N,N-dicarboxymethyl-L-glutamic acid,
25 ethylenediamine-N,N'-disuccinic acid, and their salts and mixtures, are preferred examples of compounds of formula (B).

It should be noted that the term "mixture"

means a mixture of several acids, a mixture of several salts of an acid or of salts of several acids together, or alternatively a mixture of an acid and of one or more of its salts.

- 5 Preferably, the polycarboxylic acids used are of formula (B) in which R represents a hydrogen atom or a group chosen from groups (a) to (d) and (f).

 The content of sequestering agent advantageously represents 0.0001% to 20% by weight
10 relative to the weight of the composition, more particularly between 0.001% and 10% by weight relative to the weight of the composition and preferably between 0.01% and 5% by weight relative to the weight of the composition.

- 15 The cosmetically acceptable medium generally consists of water or of a mixture of water and of one or more common organic solvents.

 Among the solvents that are suitable for use, mention may be made more particularly of alcohols such
20 as ethyl alcohol, isopropyl alcohol, benzyl alcohol and phenylethyl alcohol, or glycols or glycol ethers, for instance ethylene glycol monomethyl ether, monoethyl ether or monobutyl ether, propylene glycol and ethers thereof, for instance propylene glycol monomethyl
25 ether, butylene glycol, dipropylene glycol and diethylene glycol alkyl ethers, for instance diethylene glycol monoethyl ether or monobutyl ether, or alternatively polyols, for instance glycerol.

Polyethylene glycols and polypropylene glycols, and mixtures of all these compounds, may also be used as solvent.

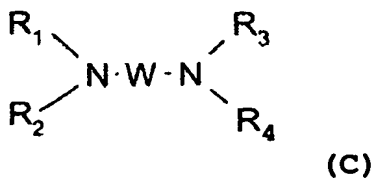
The common solvents described above usually represent, if they are present, from 1% to 40% by weight and more preferably from 5% to 30% by weight relative to the total weight of the composition.

The pH of the composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 11 approximately.

It may be adjusted to the desired value by means of acidifying or basifying agents.

Examples of acidifying agents that may be mentioned include mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid, sulphuric acid or acetic acid.

Examples of basifying agents that may be mentioned include aqueous ammonia, alkaline carbonates, alkanolamines such as monoethanolamine, diethanolamine and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (C) below:



in which W is a propylene residue optionally substituted with a hydroxyl group or a C₁-C₆ alkyl radical; R₁, R₂, R₃ and R₄, which may be identical or different, represent a hydrogen atom or a C₁-C₆ alkyl or
5 C₁-C₆ hydroxyalkyl radical.

The composition in accordance with the invention may also comprise various conventionally used adjuvants, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures
10 thereof, hair dyes, polymers, mineral thickeners, antioxidants, penetrating agents, fragrances, buffers, dispersants, conditioners, for instance cations, silicones, film-forming agents, preserving agents and stabilizers.

15 When one or more surfactants are present, preferably of nonionic, anionic or amphoteric type, their content represents from 0.01% to 30% by weight relative to the weight of the composition.

Needless to say, a person skilled in the art
20 will take care to select this or these optional additional compound(s) such that the advantageous properties intrinsically associated with the composition in accordance with the invention are not, or are not substantially, adversely affected by the
25 envisaged addition(s).

The composition according to the invention may be in various forms, such as in the form of liquids, shampoos, creams or gels, or in any other

suitable form.

In one form that is particularly preferred according to the present invention, the composition is in the form of a lightening dye shampoo comprising, in
5 a cosmetically acceptable aqueous medium.

The composition according to the invention may also contain at least one oxidizing agent. This agent may be chosen, for example, from hydrogen peroxide, urea peroxide, alkali metal bromates,
10 persalts such as perborates and persulphates, and enzymes such as peroxidases and two-electron or four-electron oxidoreductases. The use of hydrogen peroxide or enzymes is particularly preferred.

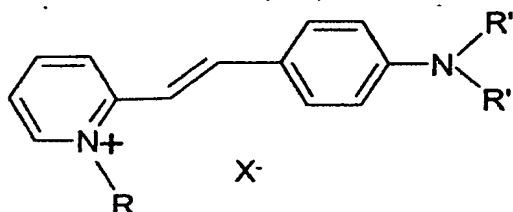
A subject of the invention is also the use,
15 for dyeing human keratin materials with a lightening effect, of a composition comprising, in a cosmetically acceptable medium, at least one fluorescent dye soluble in the said medium, and at least one complexing agent chosen from hydroxycarboxylic acids and polycarboxylic
20 acids, and the monovalent or divalent alkali metal, alkaline-earth metal, transition metal, organic amine or ammonium salts thereof, alone or as mixtures.

In the context of this use, the fluorescent compound may be chosen from the fluorescent dyes
25 belonging to the following families: naphthalimides; cationic or non-cationic coumarins; xanthenodi-quinolizines (especially such as sulphorhodamines); azaxanthenes; naphtholactams; azlactones; oxazines;

thiazines; dioxazines; monocationic or polycationic fluorescent dyes of azo, azomethine or methine type, alone or as mixtures.

Compounds that may be mentioned more particularly include the compounds of formulae F1, F2 and F3 already detailed previously.

It is similarly possible to use the compounds of structure (F4) below:



in which formula R represents a methyl or ethyl radical; R' represents a methyl radical and X⁻ represents an anion of chloride, iodide, sulphate, methosulphate, acetate or perchlorate type. An example of a compound of this type that may be mentioned is the photosensitizing dye NK-557 sold by the company Ubichem, for which R represents an ethyl radical, R' represents a methyl radical and X⁻ represents an iodide.

Everything that has been described previously regarding the natures and contents of the various additives present in the composition remains valid and will not be repeated in this section.

According to the present invention, the term "human keratin materials" means the skin, the hair, the nails, the eyelashes and the eyebrows, and more particularly coloured skin and artificially dyed or

pigmented hair.

For the purposes of the invention, the term "coloured skin" means a skin whose lightness L^* measured in the CIEL $L^*a^*b^*$ system is less than or
5 equal to 45 and preferably less than or equal to 40, given that $L^*=0$ is equivalent to black and $L^*=100$ is equivalent to white. The skin types corresponding to this lightness are African skin, Afro-American skin, Hispano-American skin, Indian skin and North African
10 skin.

For the purposes of the invention, the expression "artificially dyed or pigmented hair" means hair whose tone height is less than or equal to 6 (dark blond) and preferably less than or equal to 4
15 (chestnut-brown).

The lightening of the hair is evaluated by the "tone height", which characterizes the degree or level of lightening. The notion of "tone" is based on the classification of the natural shades, one tone
20 separating each shade from the shade immediately following or preceding it. This definition and the classification of the natural shades are well known to hairstyling professionals and are published in the book "Sciences des traitements capillaires " [Hair treatment
25 sciences] by Charles Zviak, 1988, published by Masson, pp. 215 and 278.

The tone heights range from 1 (black) to 10 (light blond), one unit corresponding to one tone; the

higher the figure, the lighter the shade.

Another subject of the present invention thus concerns a process for dyeing human keratin fibres with a lightening effect, which consists in performing the

5 following steps:

- a) the composition according to the invention is applied to the keratin fibres, for a time that is sufficient to develop the desired coloration and
10 lightening,
- b) the said fibres are optionally rinsed,
- c) the said fibres are optionally washed with shampoo and rinsed,
- d) the fibres are dried or are left to dry.

15 A subject of the present invention is also a process for colouring coloured skin with a lightening effect, in which the composition that has just been described is applied to the skin and the skin is then dried or is left to dry. Preferably, this composition
20 is not used in the presence of an oxidizing agent.

Everything that has been described previously regarding the various constituent components of the composition remains valid, and reference may be made thereto.

25 In particular, the processes according to the invention are suitable for treating human keratin fibres, and especially artificially dyed or pigmented hair, or alternatively coloured skin.

More particularly, the fibres that may be advantageously treated with the process according to the invention have a tone height of less than or equal to 6 (dark blond) and preferably less than or equal to 5 4 (chestnut-brown).

Furthermore, a coloured skin capable of being treated in accordance with the invention has a lightness L^* , measured in the CIEL $L^*a^*b^*$ system, of less than or equal to 45 and preferably less than or 10 equal to 40.

According to a first embodiment of the invention, the process of dyeing fibres with a lightening effect is performed with a composition that does not comprise oxidizing agent.

15 According to a second embodiment of the invention, the process of dyeing fibres with a lightening effect is performed with a composition comprising an oxidizing agent.

According to a first variant of these dyeing 20 processes in accordance with the invention, at least one composition as defined above is applied to the fibres, and especially the hair, for a time that is sufficient to develop the desired coloration and lightening, after which the fibres are rinsed, washed 25 optionally with shampoo, rinsed again and dried.

According to a second variant of these dyeing processes in accordance with the invention, at least one composition as defined above is applied to the

fibres, and especially the hair, without final rinsing.

According to a third dyeing process variant in accordance with the invention, the dyeing process comprises a preliminary step that consists in
5 separately storing, on the one hand, a composition according to the invention, and, on the other hand, a composition comprising, in a cosmetically acceptable medium, at least one oxidizing agent, and then in mixing them together at the time of use, after which
10 this mixture is applied to the keratin fibres, and especially the hair, for a time that is sufficient to develop the desired coloration, after which the fibres are rinsed, washed optionally with shampoo, rinsed again and dried.

15 The time required to develop the coloration and to obtain the lightening effect on the fibres, especially the hair, is about 5 to 60 minutes and more particularly about 5 to 40 minutes.

The temperature required to develop the
20 coloration and to obtain the lightening effect is generally between room temperature (15 to 25°C) and 80°C and more particularly between 15 and 40°C.

Another subject of the invention is a multi-compartment device for dyeing keratin fibres, and
25 especially the hair, with a lightening effect, comprising at least one compartment containing a composition according to the invention, and at least one other compartment containing a composition

comprising at least one oxidizing agent. This device may be equipped with a means for applying the desired mixture to the fibres, such as the devices described in patent FR 2 586 913.

5 It should be noted that the composition according to the invention, if it is used to treat keratin fibres, for example such as chestnut-brown hair, makes it possible to achieve the following results:

10 If the reflectance of the hair is measured when it is irradiated with visible light in the wavelength range from 400 to 700 nanometres, and if the reflectance curves as a function of the wavelength are compared for hair treated with the composition of the
15 invention and untreated hair, it is found that the reflectance curve corresponding to the treated hair, in a wavelength range from 500 to 700 nanometres, is higher than that corresponding to the untreated hair.

 This means that, in the wavelength range from
20 500 to 700 nanometres, and preferably from 540 to 700 nanometres, there is at least one range in which the reflectance curve corresponding to the treated hair is higher than the reflectance curve corresponding to the untreated hair. The term "higher than" means a
25 difference of at least 0.05% and preferably of at least 0.1% of reflectance.

 However, it is pointed out that there may be, within the wavelength range from 500 to 700 nanometres

and preferably from 540 to 700 nanometres, one or more ranges in which the reflectance curve corresponding to the treated fibres is either superimposable on or lower than the reflectance curve corresponding to the untreated fibres.

Preferably, the wavelength at which the difference is maximal between the reflectance curve for the treated hair and that for the untreated hair is in the wavelength range from 500 to 650 nanometres and preferably in the wavelength range from 550 to 620 nanometres.

In addition, and preferably, the composition according to the invention is capable of lightening the hair and the skin to a shade which, measured in the CIEL $L^*a^*b^*$ system, has a variable b^* of greater than or equal to 6, with a $b^*/\text{absolute value of } a^*$ ratio of greater than 1.2 according to the selection test described below.

Selection test

The composition is applied to chestnut-brown keratin fibres, more particularly the hair, at a rate of 10 grams of composition per 1 gram of chestnut-brown fibres. The composition is spread so as to cover all of the fibres. The composition is left to act for 20 minutes at room temperature (20 to 25°C). The fibres are then rinsed with water and then washed with a shampoo based on lauryl ether sulphate. They are then dried. The spectrophotometric characteristics of the

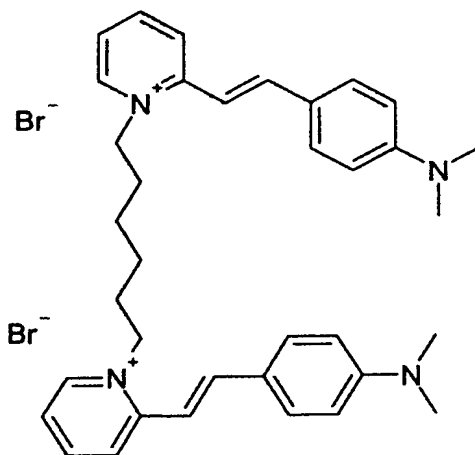
fibres are then measured in order to determine the L*a*b* coordinates.

In the CIEL L*a*b* system, a* and b* indicate two colour axes: a* indicates the green/red colour axis (+a* is red, -a* is green) and b* indicates the blue/yellow colour axis (+b* is yellow and -b* is blue); values close to zero for a* and b* correspond to grey shades.

The examples that follow are intended to illustrate the invention without, however, limiting its scope.

EXAMPLES

Fluorescent compound



93 g of 2-picoline are reacted with 120 g of 1,6-dibromohexane in dimethylformamide at 110°C for 5 hours.

The precipitated product is recovered and filtered off.

109 g of the product obtained above are

dissolved in methanol and 82.82 g of p-dimethylamino-benzaldehyde are added in two portions, in the presence of pyrrolidine.

The mixture is then left for 30 minutes.

- 5 The product is recovered in precipitated form.

Analysis by mass spectroscopy: 266.

Elemental analysis: C: 62.43%; H: 6.40%; Br: 23.07%; N: 8.09%.

- 10 The formula is as follows: $C_{36}H_{44}N_4 \cdot 2Br$.

Compositions

Composition	1	2
Fluorescent compound	1%	1%
Mucic acid	0.2%	-
N-lauroylethylenediamine-N,N',N'-triacetic acid	-	0.2%
pH agent qs	pH 7	pH 7
Distilled water	qs 100%	qs 100%

- 15 Dyeing

Each composition is applied to a lock of natural chestnut-brown hair (tone height 4) with a leave-in time of 20 minutes.

- 20 The lock is then rinsed and dried under a hood for 30 minutes.

A marked lightening effect is obtained on the

locks.